

CHARGE TRANSFER COMPLEXES OF COAL-DERIVED ASPHALTENES

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INTRODUCTION

Coal-derived asphaltenes are thought to be key intermediates in the conversion of coal to oil (1). A model, based on x-ray diffraction studies (2), has been proposed to describe the macrostructure of associated asphaltenes in the solid state (3). The state of association of these species in benzene and tetrahydrofuran solution has been studied by vapor pressure osmometry, and molecular weights have been reported as a function of concentration (4). Evidence has been presented recently in the literature supporting a hydrogen-bonding donor-acceptor association in solution (5-7). Previously the mechanism of association of petroleum asphaltenes (8-10), and coal and chars (11) was described in terms of charge transfer donor-acceptor forces. A study of the properties of iodine-petroleum asphaltene complexes was carried out, and led to useful information on the structure of petroleum asphaltenes (12). It was therefore decided to synthesize charge transfer complexes of coal-derived asphaltenes, and to study their properties by a variety of physical and analytical techniques.

EXPERIMENTAL

Coal-derived asphaltenes were separated by solvent fractionation (13, 14) from coal liquids produced in five major demonstration liquefaction processes: Synthoil, HRI H-Coal, FMC-COED, Catalytic Inc. SRC, and PAMCO SRC. The asphaltenes were further separated into three fractions by exhaustive solvent elution chromatography on silica gel using the solvents: benzene, diethyl ether, and tetrahydrofuran. The benzene and diethyl ether eluted fractions, known to contain a higher and lower proportion of basic asphaltene molecules (13), were used in addition to starting asphaltene to form some of the complexes.

Complexes were formed by mixing benzene solutions of the asphaltenes (~50 g/l) with benzene solutions of either iodine or tetracyanoethylene (freshly sublimed reagent grade) in the approximate mole ratios, asphaltene/acceptor = 0.7 - 1.0/1. A precipitate forms rapidly. It was filtered, washed with benzene and dried overnight at 40°C/2mm Hg.

The dark brown to black I₂-asphaltene complexes are relatively insoluble in benzene, carbon disulfide, and pentane, and slightly to moderately soluble in chloroform and tetrahydrofuran. The brown-black TCNE-asphaltene complexes are only moderately soluble in THF.

Analyses were performed by the ELEK Microanalytical Laboratories, Torrance, California. Iodine was determined gravimetrically after nitric acid oxidation in the presence of silver nitrate; nitrogen was determined by the Dumas procedure. Molecular weights were measured in THF with a Mechrolab Model 301A Vapor Pressure Osmometer. Infrared spectra were determined as KBr disks on a Beckman Acculab 6 IR. Ultraviolet-visible spectra were run in either chloroform or tetra-

hydrofuran solution on a Beckman Model 25 Spectrophotometer. X-ray diffraction measurements were made with a General Electric XRD-6 x-ray diffractometer with a $\text{CuK}\alpha$ radiation source (15). Electron spin resonance spectra were taken with a Varian E-12 x-band spectrometer. Resistivity measurements were carried out at 25°C over the pressure range 10-3000 atmospheres by use of a cell and procedure described by Hadek (16).

RESULTS AND DISCUSSION

Composition of Complexes

Analytical data for I_2 -asphaltene and TCNE-asphaltene complexes are presented in Tables I and II. The mole ratios of asphaltene to iodine are approximately 1 to 1 with the exception of the FMC-COED - I_2 complex which afforded a tar-like material initially instead of a precipitate. The mole ratios of asphaltene to TCNE are more widespread, but are closer to 2 to 1. The mole ratio calculations are based on the assumption that the molecular weight of the asphaltene portion of the complex is the same as the molecular weight of the starting asphaltene, which may not be strictly correct.

Ultraviolet-Visible Spectra of Complexes

Measurement of the UV-Visible spectrum of I_2 -asphaltene complexes in THF or CHCl_3 (Fig. 1) leads to the observation of a new band at ≈ 295 nm and new shoulder at ≈ 355 nm. Neither of these absorptions is observed in the free components. These bands are presumed to be charge-transfer absorption bands of the iodine-asphaltene complex. The nature of the donor interaction of the asphaltene may be either via the electrons of the π -orbitals, or via the non-bonded, lone pair electrons in atomic orbitals of n donors such as nitrogen or oxygen bases.

Measurement of the UV-Visible spectrum of TCNE-asphaltene complexes in THF (Fig. 2) leads to the observation of new bands at 406 and 425 nm not found in the free components. These bands are presumed to be charge-transfer absorption bands of the donor asphaltene molecules and the π -acceptor TCNE.

Infrared Spectra

Asphaltene-iodine samples were run as KBr disks, and infrared spectra were obtained directly, and differentially of asphaltene-iodine complexes versus reference asphaltene. No C-I stretching frequencies were observed in the 400-600 cm^{-1} region, and no aromatic- I_2 bands in the 992 cm^{-1} to 1200 cm^{-1} region (17, 18).

Asphaltene-TCNE complexes were run in KBr disks and the infrared spectra compared with those of the free components, and physical mixtures of the free components. The most obvious changes are in the TCNE doublet at 2200 cm^{-1} which changes to a singlet, and in the appearance of a prominent new band at 1500 cm^{-1} .

X-Ray Diffraction

The x-ray diffraction patterns of asphaltenes show diffuse bands typical of mesomorphic or semicrystalline substances (2): the (002) band is attributed to the interplanar spacing between condensed aromatic rings of ≈ 3.5 Å; the gamma band is attributed to the spacing between disordered aliphatic chains or alicyclic rings of ≈ 4.6 Å (Fig. 3).

X-ray analysis of petroleum asphaltene-iodine complexes indicates a low degree of order exists within these complexes (12). The (002) band disappears on forming a petroleum asphaltene-iodine complex, and a new band at 8.7 Å appears. These observations were rationalized by assuming that the layered structure of the asphaltene was expanded from 3.5 Å to 8.7 Å by intercalation of a molecule of iodine between the aromatic layers of the asphaltene.

In the case of coal-derived asphaltene-iodine complexes, the x-ray results show the loss of both the (002) and the (γ) bands, but no new peak is formed at ≈ 8.7 Å (Fig. 3). This result may be interpreted by assuming that iodine molecules are not sandwiched between the aromatic layers, and that the asphaltene-iodine complexes are no longer ordered in the solid state but have become amorphous.

The x-ray diffraction patterns of asphaltene-TCNE complexes have been measured. The diffraction patterns show a large increase in the intensity of the 002-Band of the TCNE complex, which is associated with the interplanar spacing between condensed aromatic rings, and the appearance of a new band for Synthoil-TCNE, which corresponds to a larger distance of ≈ 11 to 14 Å. The x-ray diffraction patterns were analyzed, and aromaticity and x-ray crystallite parameters determined (Table III). The results indicate structural differences between the asphaltene base fractions (Et_2O eluted from silica gel) and their TCNE complexes. The aromaticity, f_a , increases from asphaltene base fractions to complexed products. The distance through the aromatic sheets, L_a , and the number of layers per cluster M are increased after complexing. However, the diameter of the aromatic sheet, L_a , shows a decrease or no change. The spacing between aliphatic chains or sheets, d_y , and the spacing between the aromatic sheets, d_m , do not show much change. These results, and the appearance of the new bands at 11-14 Å, may be rationalized in terms of asphaltene-TCNE complex clusters such as the ones shown in Fig. 4. If the TCNE molecules are complexed on top and below the asphaltene sheets, instead of intercalated between the asphaltene sheets, then an increase of L_a would be observed, but an increase in d_m or d_y would not be required. L_a , the average diameter of the aromatic sheet would be expected to be lower if a smaller TCNE molecule in the complex represented a pseudo-aromatic sheet. M , the effective number of aromatic sheets would be expected to be larger. The new bands corresponding to an 11-14 Å separation in Synthoil-TCNE could represent the distance between TCNE molecules in the complexes. The aromaticity, f_a , would be expected to increase in the complexes due to the pseudo-aromatic character of the TCNE π -system.

ESR Spectra

ESR parameters of Synthoil asphaltenes and their I_2 and TCNE complexes are presented in Table IV. The spin intensity is seen to be significantly larger in the complexes than in the uncomplexed asphaltenes. This may be indicative of low lying triplet states in the complexes which can be populated at room temperature.

Conductivity

The resistivities of a series of asphaltenes and their I_2 and TCNE complexes have been measured, and range between about 3×10^9 - 3×10^{10} ohm-cm at 25°C and 10 atm. pressure. In each case the resistivity of the complex is lower than that of the parent asphaltene, but not by more than an order of magnitude. These resistivities may be contrasted with those obtained for petroleum asphaltenes which exhibit higher values, in the insulator range, of 10^{16} - 10^{17} ohm-cm at 25°C, but upon addition of iodine, the resistivities of the complexes formed decrease by about one million-fold (12).

The effect of pressure, over the range 10-3000 ATM., on resistivity is shown in Fig. 5. The resistivity of the uncomplexed asphaltenes is seen to remain essentially constant, however, two of the asphaltene-I₂ complexes afford a decrease in resistivity over the same pressure range. This is consistent with electronic conduction.

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Table I. Analytical Data for I₂-Asphaltene Complexes

Asphaltene	VPO ^a MW	% Iodine	Asphaltene ^b /I ₂
Synthoil	560	35.02	0.84
HRI H-Coal	492	28.13	1.33
FMC-COED ^c	375	22.00	2.38
PANCO SRC ^d	363	38.36	1.12
CAT. INC. SRC	483	32.72	1.08
CAT. INC. Benzene Eluted 511		30.34	1.15
CAT. INC. Et ₂ O Eluted ^e	459	34.03	1.08

^a Average of infinite dilution MW's in benzene and tetrahydrofuran of starting asphaltenes. ^b Mole ratios calculated assuming MW of asphaltene portion of complex is the same as the MW of the starting asphaltene. ^c A tar formed on mixing the asphaltene/I₂ solutions. ^d From Filter Feed. ^e Eluted from Silica Gel.

Table II. Analytical Data for TCNE-Asphaltene Complexes

Asphaltene ^a	VPO ^b MW	ZN Complex - ZN Starting Asphaltene	Asphaltene ^c /TCNE
Synthoil	522	5.08 ^d , 5.21	1.87, 1.82
HRI H-Coal	496	5.13	1.95
FMC-COED	383	5.48	2.34
PANCO SRC	532	3.76	2.56
CAT. INC. SRC	459	7.61	1.33

^a Asphaltene eluted from Silica Gel with Et₂O after exhaustive elution of asphaltene with benzene. ^b Average of infinite dilution MW's in benzene and tetrahydrofuran of starting asphaltenes. ^c Mole ratios calculated assuming MW of asphaltene portion of complex is the same as the MW of the starting asphaltene. ^d Two different preparations.

Table III. X-Ray Analysis of Synthoil Asphaltene Basic Fraction and Synthoil Asphaltene-TCNE Complex

	Synthoil Asphaltene Et ₂ O Eluted	Synthoil Asphaltene Et ₂ O Eluted-TCNE Complex
f_a^1	0.64	0.72
d_a^2	3.47	3.46
d_y^2	4.52	4.52
l_c^2	12.1	13.8
l_a^3	10.0	10.1
l_a^4 (11) band	11.4	11.9
M^5	4	5

$f_a = C_a/C_{total} = A_{002}/A_{002} + A_y$, d_a^2 = interlayer distance, d_y = interchain distance, l_c^2 = diameter of the aromatic clusters perpendicular to the plane of the sheets, l_a^3 = diameter of the aromatic sheets from Diamond's Curve, l_a^4 = diameter of the aromatic sheets from Scherrer's Eq., all values in Å. ⁵ Effective number of aromatic sheets associated in a stacked cluster.

Table IV. ESR Parameters of Asphaltenes and Asphaltene Complexes^a

Sample	g-Value ^b	Intensity, N ^b (x10 ⁻³) Spins/g	Line Width ΔH, Gauss
Synthoil Asphaltene	2.0030	1.4	6.4
Synthoil Asph. Et ₂ O Eluted	2.0031	0.8	6.8
Synthoil Asph.-I ₂ Complex	2.0032	28.8	9.8
Synthoil Asph. Et ₂ O Eluted-TCNE Complex	2.0029	5.5	8.2

^a Solid samples. ^b Measured relative to DPPH.

FIG. 1. UV-VIS. SPECTRA OF I_2 , SYNTHOIL ASPHALTENE, AND SYNTHOIL ASPHALTENE- I_2 COMPLEX IN $CHCl_3$

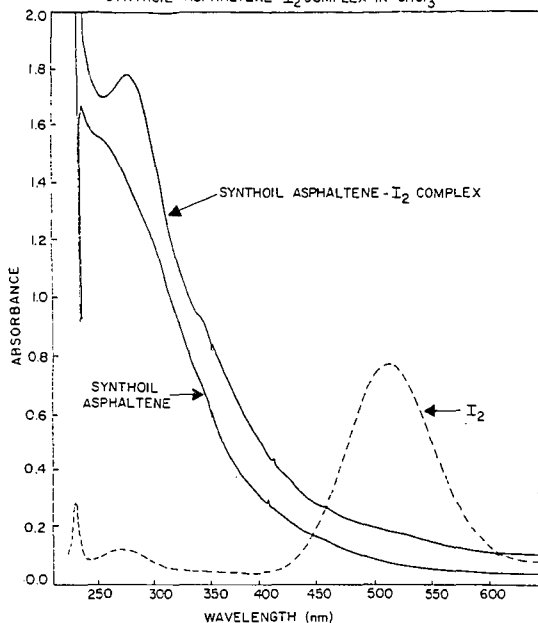


FIG. 2. UV-VIS. SPECTRA OF TCNE, SYNTHOIL ASPHALTENE, AND SYNTHOIL ASPHALTENE-TCNE COMPLEX IN THF

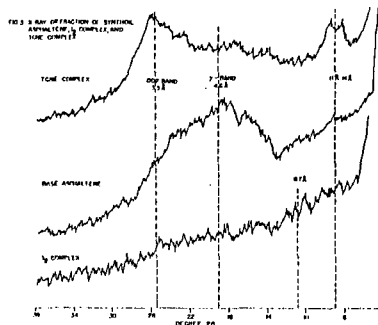
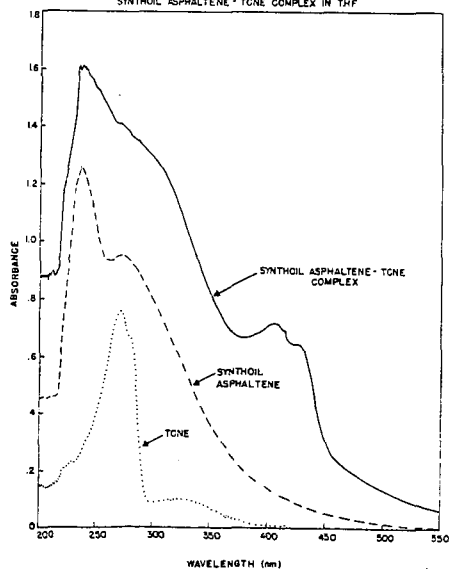


FIG. 4. CROSS-SECTIONAL VIEW OF SYNTHOIL ASPHALTENE BASE FRACTION AND SYNTHOIL ASPHALTENE-TCNE MODEL COMPLEX CLUSTERS

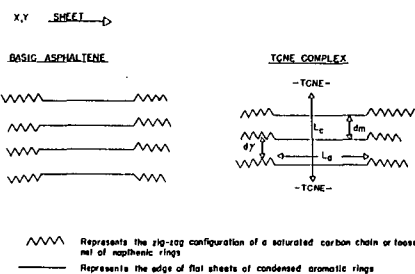


FIG. 3. RESISTIVITY OF CAT. INC. SRC. ASPHALTENE, ASPHALTENE DERIVATIVES, ASPHALTENE COMPLEXES VS. PRESSURE

